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# INVESTIGATION TO DEVELOP OR INNOVATE METHODS FOR THE REMOVAL OF OXYGEN FROM COALS

## PHASE II

FINAL REPORT

BY

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SNC

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ABSTRACT

Several inorganic reducing agents ($FeSO_4$, $Na_2S_2O_3$, NaSH, $Na_2SO_3$, $NaNO_2$ and $N_2H_4$) have been tested to see if they reduce the oxygen content of coal. It was found that oxygen content of coals decreased when they were heated in water alone (blank runs). The treatment with the reducing agents containing sulphur did not increase the oxygen removal over that achieved in the blank runs. However, it appears that the ferrous salt catalytically deoxygenated both the lignite and bituminous coals presumably by decarboxylation.

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## 1.0 INTRODUCTION

All ranks of coal contain a certain amount of oxygen chemically bound in the coal molecules. The percentage oxygen decreases as the rank increases. Figure 1, redrawn from Page 267 of Lowry (1) shows the general relationship by which the various oxygen functional groups found in coals decrease as the rank of the coal increases.

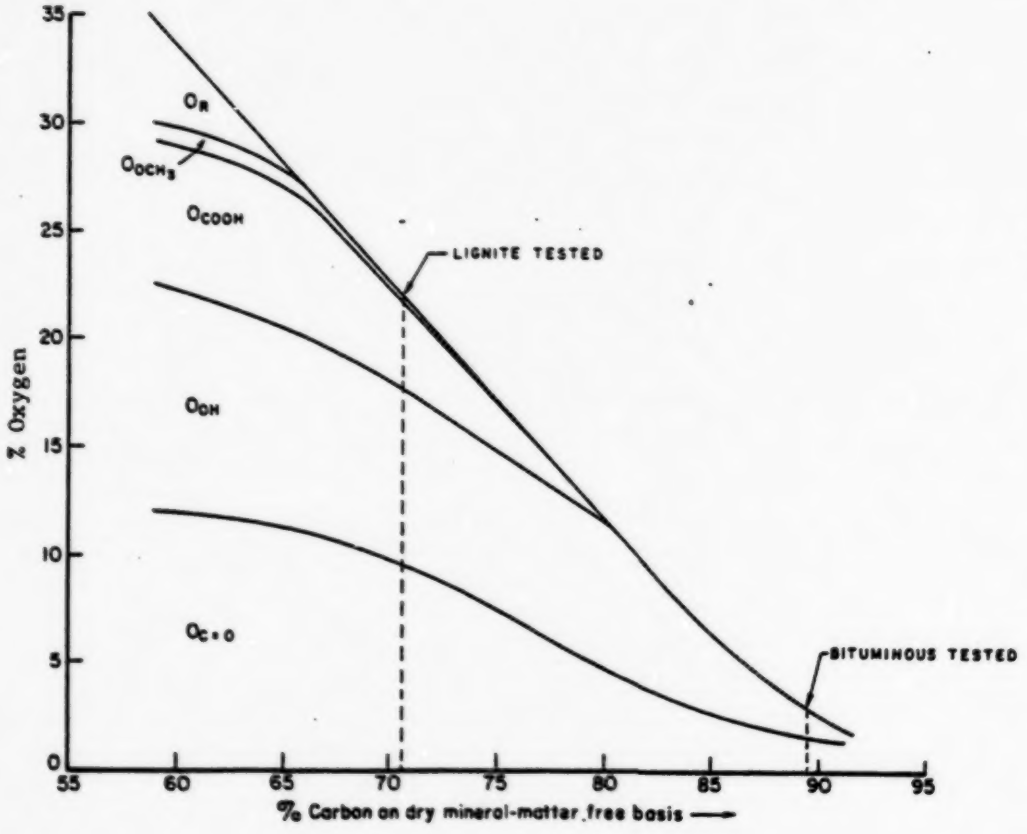


Figure 1 Functional oxygen groups of vitrain according to rank.

1.0 INTRODUCTION (cont'd)

Oxygen in coal lowers its fuel value and hence lowers the coals' commercial value. If coal is to be liquefied by hydrogenation, the oxygen present has also to be hydrogenated. The end product in this case is water which has no fuel value. In essence the hydrogen is wasted if it is used to remove oxygen from coal. Clearly, if an energy efficient process of removing oxygen from coal could be developed it would have considerable merit and a wide commercial application

This project was initiated by CANMET which solicited proposals for "Innovative Methods for the Removal of Oxygen from Coals". SNC suggested that one approach that would be worthwhile investigating was to try a series of inorganic reducing agents to see if they had effect in removing the oxygen.

To be more precise, it was hypothesized that, the organic oxygen in coal could be removed by treating it at a moderately elevated temperature with an aqueous solution of an inorganic reducing agent of sufficient reducing strength.

As a measure of the reducing strength of the reducing agents, the standard free energy was used. The following reducing agents were suggested for the tests in the decreasing order of their reducing strengths.

| | $\Delta_{F^\circ}$ kcal/g mole |
|---|---|
| $1/2\ N_2H_4 + 1/2\ O_2 \longrightarrow 1/2\ N_2 + H_2O$ | 72.5 |
| $Na_2SO_3 + 1/2\ O_2 \longrightarrow Na_2SO_4$ | 58.5 |
| $NaHS + 1/2\ O_2 \longrightarrow NaOH + S$ | 50.0 |
| $Na_2S_2O_3 + 1/2\ O_2 \longrightarrow Na_2S_2O_4$ | 10.8 |
| $3FeSO_4 + 1/2\ O_2 + H_2O \longrightarrow Fe_2(SO_4)_3 + Fe(OH)_2$ | 2.8 |

## 1.0 INTRODUCTION (cont'd)

The experimental work for the present investigation was performed at Technitrol Laboratories Inc.

It should be pointed out that the present investigation was exploratory in nature and the amount of work done was modest. Based on these data, certain trends have been observed which are presented in the subsequent sections of this report. However, some these trends predicted may have stretched the limits of the accuracy, and predictability of the analysis. Nevertheless, there is a logical explanation for all the effects which were observed. The observations are consistent with what is known about the structure of coal. Although the results are not quantitatively precise, they are qualitatively correct.

## 2.0 EXPERIMENTAL PROCEDURE

### 2.1 Coals Selection

Two types of coals having different oxygen contents were selected for the present investigation. A master sample of high volatile bituminous coal was obtained from the Fording Coal, at Fording, B.C. and a master sample of lignite coal was acquired from M & S Mine, Bienfait, Saskatchewan.

### 2.2 Coal Samples Preparation

The coal master samples were crushed and ground to a particle size of about 125 μ . After screening with No. 100 screen, each powdered coal sample was stored in a closed plastic container.

### 2.3 Reducing Agents Employed

The reducing agents listed in section 1 were used.

### 2.4 Experimental Scheme

The experimental scheme presented in Figure 2 shows the sequence of experimental steps along with the designation of the analyzed products.

#### 2.4.1 Deoxygenation Test

The experimental equipment consisted of an autoclave, manufactured by Autoclave Engineers. Its nominal capacity was 2 gallons (9.1 L). The design pressure and temperature of the autoclave were 5000 psi and 650°C respectively. The autoclave was installed on a rocking mechanism. During the runs, the autoclave was continuously agitated. The pressure inside the autoclave was measured by a calibrated pressure gauge mounted directly on the autoclave. The temperature was measured by thermocouple and recording potentiometer.

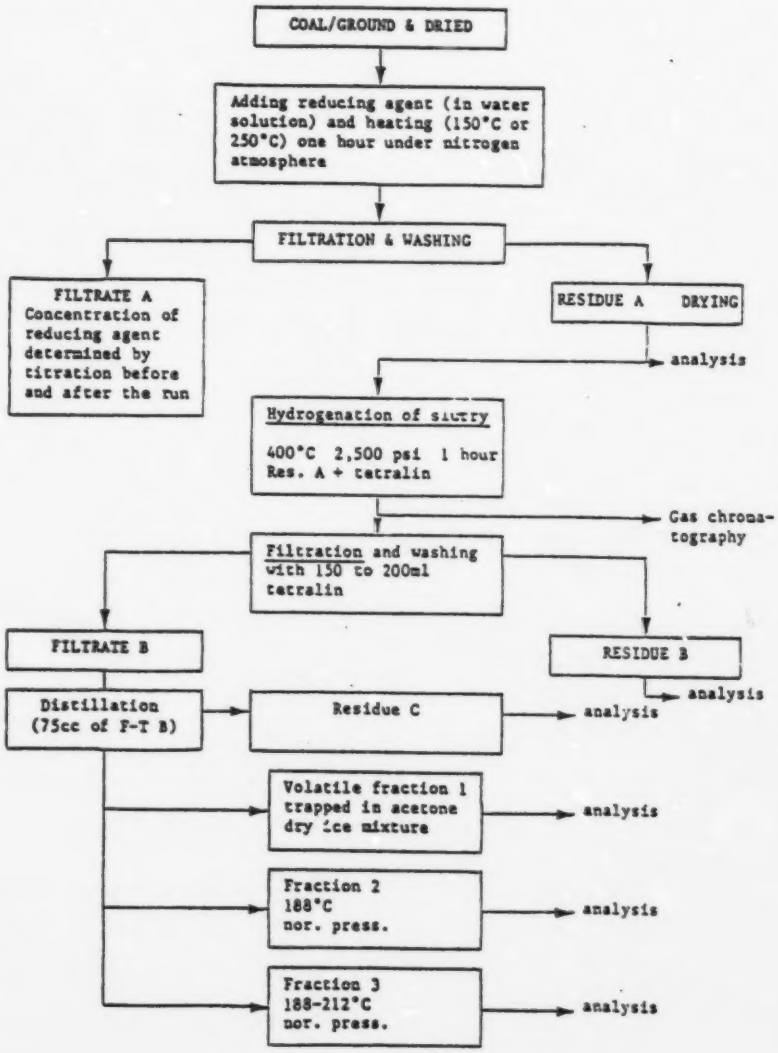


Figure 2 Coal Treatment Scheme

## 2.0 EXPERIMENTAL PROCEDURE (cont'd)

### 2.4.1 Deoxygenation Test (cont'd)

A coal sample to be investigated was first oven dried overnight at 110°C. After drying, 50 g sample of coal was placed in an open flask along with demineralized water (blank run) or with a aqueous solution containing the particular reducing agent. The flask was placed in the autoclave. After closing, the autoclave was purged with nitrogen so as to carry out the reduction in an inert atmosphere.

The temperature was raised to 150°C or 250°C and held there for a period of one hour after which the autoclave was cooled to the ambient temperature. The gases were then vented to the atmosphere. The solid product (residue A) was filtered out, washed and oven dried overnight at 110°C. The filtrate (filtrate A) was titrated to determine the weight of the reducing agent. Thus, from the amount of the reducing agent initially put in the water to prepare its solution and the amount of the reducing agent in the filtrate A, the weight of the reducing agent consumed was determined.

### 2.4.2 Hydrogenation Test

In this test, the residue A (from the blank runs as well as from the deoxygenation runs) was hydrogenated at the temperature of 400°C and 2500 psi pressure. The weight of residue A hydrogenated was 20 g except in the first few runs when the weight of the sample was 50 g. A slurry of 30 wt % residue A in tetralin was placed in an open flask and the flask was placed in the autoclave. The autoclave was then pressurized to 1000 psi with hydrogen at room temperature. The temperature was then raised to 400°C and the pressure of the hydrogen increased to 2500 psi. The autoclave was kept at that temperature for an hour, after which it was cooled to room temperature. The gaseous product was then analyzed in a gas chromatograph. The autoclave was kept at that temperature and

## 2.0 EXPERIMENTAL PROCEDURE (cont'd)

### 2.4.2 Hydrogenation Test (cont'd)

pressure for an hour, after which it was cooled to room temperature. The gaseous product was then analyzed in a gas chromatograph. The autoclave was then vented through a gas meter and a drying tube to measure the amount of gaseous products and to trap any water formed during the reaction.

The liquid product was filtered under vacuum and the collected filter cake (residue B) was thoroughly washed with 150 to 200 mL. of tetralin to remove any liquid product adhering to the solids.

A portion (75 mL) of the resulting filtrate (filtrate B) was distilled to yield three fractions (Figure 2) and a bottom product (residue C).

## 3.0 RESULTS AND DISCUSSIONS

The results of the experiments carried out are listed in Tables 1 - 12. Table 1 gives the analyses of the feed coals. Tables 2 - 3 give the deoxygenation results for lignitic coals. Tables 4 - 7 present the hydrogenation results for lignitic coals. Table 8 presents the deoxygenation results for bituminous coal and Table 9 - 12 present hydrogenation experiment results for bituminous coal.

### 3.1 General

It is known that low rank coals (lignite and subbituminous) when heated in the temperature range of 300 - 330°C produce a solid product with an increased heating value per unit mass and an insignificant loss in total heating value. A previous study (2) suggests that heating a lignite coal slurry in water at 300 - 330°C for one hour lowers its oxygen and ash content substantially. To eliminate this effect in the present study, blank runs were carried out. Thus, comparing the results of deoxygenation runs with the blank runs, the effectiveness of the chemical reducing agent during the experiments could be determined.

The degree of homogeneity of the coal samples, the accuracy and reproducibility of the analytical results have not been established. These considerations suggest caution in interpreting the results of this investigation.

### 3.2 Deoxygenation Treatment for Lignitic Coal

#### 3.2.1 Calculations to Account for the Entrapment of Reducing Agents in Residue A of the Lignite.

It will be noticed in Table 2 that when the lignite was treated with sulphur containing reducing agents, both the sulphur content and the ash content of residue A increased. Residue A was thoroughly washed and the washings were titrated to find the amount of reducing

Table 1 Analyses of the Feedstocks
Basis: Moisture Free

| Type of Coal | Bituminous | | Lignite | |
|---|---|---|---|---|
| **Proximate Analysis, wt%** | | | | |
| Ash | 21.4 | | 10.70 | |
| Volatile | 18.9 | | 41.00 | |
| Fixed Carbon | 60.0 | | 48.30 | |
| **Ultimate Analysis, wt%** | | | | |
| | | DAF | | DAF |
| C | 69.90 | 89.18 | 64.00 | 71.82 |
| H | 3.84 | 4.90 | 3.60 | 4.04 |
| N | 1.11 | 1.42 | 1.25 | 1.40 |
| S | 0.30 | 0.38 | 0.56 | 0.63 |
| O (By difference) | 3.23 | 4.12 | 19.70 | 22.11 |
| Ash | 21.4 | - | 10.70 | |

3.0 RESULTS AND DISCUSSIONS (cont'd)

3.2.1 Calculations to Account for the Entrapment of Reducing Agents in Residue A of the Lignite (cont'd)

agent consumed. Therefore this observation of increased sulphur and ash may not be due to simple physical retention of the reducing agent but can only be explained by a chemical reaction which bound the reducing agent to the coal or its ash. It is a well-known fact that sodium sulphite forms an addition compound, with ketones which contain a methyl group adjacent to the carbonyl group and with all aldehydes. With simple aldehydes and ketones these addition products can be crystallized. The crystalline addition is often used to purify carbonyl substances. The chemistry of the other sulphur reducing agents is not so well understood but from the significant increase of the sulphur content in the residue A , it can be deduced that some of the reducing agent is being chemically bound.

It should be noted that the entrapment or binding of the reducing agent occurred with the lignite and only to a minor extent with the bituminous coal.

The point to be established in these experiments is how much, if any, oxygen was removed from the original coal by the treatment with the various reducing agents. The oxygen was found by difference after determining the percentages of the ash, carbon, hydrogen, nitrogen and sulphur. If, (for example), the sodium sulphite reacts with the carbonyl groups, the sulphur contained in the addition compound is reported as sulphur in the residue A. In addition,when the material is ashed, the corresponding amount of some inorganic material (for example,sodium oxide) is found in the ash.
Both these additional weights must be found and subtracted because if they are not, then the value for the oxygen which is found by

Table 2 Deoxygenation Results for Lignitic Coal

Analysis of Residue A - As-Received and Uncorrected

| Run No. | Red. Ag. | Temp. of Red. °C | Red. Ag. Consumed G | Analyses of Residue A', wt% | | | | | | O/C | H/C |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Ash | C | H | N | S | O (Diff) | Atomic | Ratios |
| Feed Coal | - | - | - | 10.7 | 64.0 | 3.60 | 1.25 | 0.56 | 19.7 | 0.23 | 0.68 |
| 6 | None | - | - | 13.0 | 66.6 | 4.00 | 1.30 | 0.54 | 14.6 | 0.16 | 0.72 |
| 11 | None | - | - | 13.75 | 65.3 | 3.71 | 1.30 | 0.55 | 15.3 | 0.17 | 0.68 |
| 31 | $Na_2SO_3$ | 135-160 | 4.1 | 21.33 | 61.6 | 3.20 | 1.35 | 2.60 | 9.93 | 0.12 | 0.62 |
| 29 | $Na_2SO_3$ | 240-260 | 4.8 | 18.63 | 63.0 | 3.14 | 1.23 | 2.02 | 12.00 | 0.14 | 0.60 |
| 32 | $Na_2SO_3$ | 245-262 | 75.1 | 21.20 | 60.0 | 3.14 | 1.35 | 2.47 | 11.80 | 0.15 | 0.63 |
| 15 | $Na_2S_2O_3$ | 146-159 | 3.6 | 16.40 | 62.2 | 3.64 | 1.18 | 2.14 | 14.45 | 0.17 | 0.70 |
| 25 | $Na_2S_2O_3$ | 245-265 | 2.0 | 13.70 | 62.1 | 3.68 | 1.30 | 1.30 | 17.86 | 0.22 | 0.71 |
| 19 | NaHS | 140-173 | 3.8 | 21.85 | 58.9 | 3.64 | 1.21 | 2.12 | 12.03 | 0.15 | 0.74 |
| 21 | NaHS | 245-265 | None | 22.00 | 62.5 | 3.62 | 1.36 | 2.37 | 8.25 | 0.10 | 0.70 |
| 16 | $FeSO_4$ | 148-227 | None | 15.2 | 69.4 | 3.96 | 1.18 | 1.7 | 8.56 | 0.09 | 0.68 |
| 26 | $N_2H_4$ | 215-275 | 13.8 | - | 61.0 | 4.2 | 5.0 | - | - | - | 0.83 |

Table 3 Corrected Values of Deoxygenation Results for Lignitic Coal

| Run No. | Red. Ag. | Temp. of Red. °C | Red. Ag. Consumed G | Analysis of Residue A, wt% | | | | | | O/C | H/C |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Ash | C | H | N | S | O(Diff) | Atomic | Atomic |
| Feed Coal | - | - | - | 10.7 | 64.0 | 3.6 | 1.25 | 0.56 | 19.7 | 0.23 | 0.68 |
| 6 | None | - | - | 13.0 | 66.6 | 4.0 | 1.39 | 0.54 | 14.6 | 0.16 | 0.67 |
| 33 | None | - | - | 13.75 | 65.3 | 3.4 | 1.30 | 0.55 | 15.3 | 0.18 | 0.62 |
| 31 | $Na_2SO_3$ | 135-160 | 4.1 | 13.375 | 67.15 | 3.5 | 1.47 | 0.545 | 13.97 | 0.156 | 0.62 |
| 29 | $Na_2SO_3$ | 240-260 | 4.8 | 13.375 | 66.97 | 3.34 | 1.30 | 0.545 | 14.47 | 0.162 | 0.60 |
| 32 | $Na_2SO_3$ | 245-262 | 75.1 | 13.375 | 65.04 | 3.40 | 1.46 | 0.545 | 16.18 | 0.187 | 0.63 |
| 35 | $Na_2S_2O_3$ | 146-159 | 3.6 | 13.375 | 64.75 | 3.79 | 1.23 | 0.548 | 16.30 | 0.189 | 0.73 |
| 25 | $Na_2S_2O_3$ | 245-265 | 2.0 | 13.375 | 63.30 | 3.75 | 1.325 | 0.545 | 17.71 | 0.210 | 0.71 |
| 19 | NaHS | 140-173 | 3.8 | 13.375 | 60.81 | 3.16 | 1.25 | 0.545 | 20.86 | 0.257 | 0.62 |
| 21 | NaHS | 245-265 | None | 13.375 | 64.60 | 3.74 | 1.41 | 0.554 | 16.34 | 0.190 | 0.69 |
| 16 | $FeSO_4$ | 148-227 | None | 13.375 | 71.16 | 4.06 | 1.21 | 0.545 | 9.65 | 0.102 | 0.68 |
| 26 | $N_2H_4$ | 235-275 | 13.8 | - | 61.0 | 4.2 | 5.0 | - | - | | |

## 3.0 RESULTS AND DISCUSSIONS (cont'd)

### 3.2.1 Calculations to Account for the Entrapment of Reducing Agents in Residue A of the Lignite (cont'd)

difference will appear to be too low. If the correction is not made, one could falsely conclude that oxygen had been removed by the chemical agent, which might not be the case. The details of the calculation used to make this correction are given in Appendix A. It is sufficient to note here that all the sulphur in excess of that found in the blank runs (no reducing agent used) was assumed to have come from the reducing agent and hence subtracted from the sulphur value.

In addition,the oxidation product of the reducing agent is found in the ash. This was also determined and any excess over that found in the test run where no reducing agent was used was assumed to come from the reducing agent and subtracted from the ash value.

Using these corrections,Table 3 was derived.

### 3.2.2 Lignite Treatment with Water (blank run)

It has been previously shown by Elliot (2) and Liebnitz et al. (1,3) that heating lignite in water decreased its oxygen content. Similar results (4) have been observed by heating lignite and peat, in an inert atmosphere to 300 to 400°C. The oxygen is eliminated as $CO_2$.

The same effect was observed in this work. Compare the analysis of runs 6 and 33 with the analysis of the original coal. The oxygen content has decreased from 19.7% to 14.8%. About 25% of the oxygen has been removed by simply heating the coal to 150°C in the presence of water. It was concluded in the references cited above (1,2,3) that $CO_2$ was being evolved. This investigation also indicates that this effect occured.

3.0 RESULTS AND DISCUSSIONS (cont'd)

3.2.3 Treatment with a solution of Ferrous Sulphate

This treatment reduced the oxygen content of the lignite considerably more than simply heating in water. It is important to note that none of the reducing agent was consumed.

The oxygen content was reduced to 9.05% as compared to 19.7% in the original coal, about a 51% reduction. This fact along with the observation that no significant quantity of $FeSO_4$ was consumed in the treatment indicates the catalytic decarboxylation through the removal of $CO_2$. There does not appear to be any reference in the literature to the fact that ferrous salts aid in the decarboxylation of coal. However it has been reported by Royals (5) that certain metal salts, notably copper salts act catalytically to decarboxylate aromatic acids. Assuming that the treatment with ferrous salt removed all the carboxyl oxygen, a calculation was made to determine the amount of carboxyl functional group present in the coal. Appendix C gives the details. It was found that 58.8% of the original oxygen atoms in the coal exist as carboxyl functional groups. Whitehurst et al. (6) have reported that 46% of the oxygen in the coal is in the form of carboxyl functional group (for coal with 71% carbon on a dry basis). Since the calculated amount of carboxyl groups is higher than reported elsewhere, we can conclude that they were all removed by the catalytic action of the ferrous ion. It would be overly speculative to conclude that other oxygen functionalities were also removed, but this point should be investigated in subsequent work.

3.2.4 Treatment with Other Reducing Agents

In Table 3, which gives the corrected analysis of the elements in the residue A, it can clearly be seen that only in the case of treatment with ferrous sulphate resulted in an analysis of oxygen less than

3.2.4 Treatment with Other Reducing Agents (cont'd)

when the lignite was treated by heating it in water. The same effect is seen by comparing the figures for the O/C ratio. These figures are shown on the graphs in Figure 3.

It appears that none of the reducing agents were able to remove any oxygen. All the reducing agents were dissolved in water. The amount of oxygen removed is about equivalent to heating in water with no reducing agent.

3.2.5 Treatment with Hydrazine

For lignite treated with hydrazine, no simple explanation is adequate. The increase of nitrogen in the residue must be attributed to the formation of hydrazone or azine or some other nitrogen compound. Nitrogen complex formation is logical since the material containing nitrogen did not evaporate during the drying operation and some of it was still present in residue C. Assuming hydrazone formation, 2.7g of oxygen would have been removed. Azine formation would have removed 5.4g oxygen. Azine formation cannot account for the gain in hydrogen and total weight and hydrazone formation cannot account for the net increase in weight.

The treatment with $NaNO_2$ resulted in decomposition of the reducing agent. Hence no analysis of the residue could be carried out.

3.3 Deoxygenation Treatment for Bituminous Coal

Bituminous coal reacted much differently than the lignite. The first point of difference noted was that bituminous coal did not in general react to bind the sulphur as did lignite. Only in the case of Run 5, ($Na_2SO_3$ at 150°C) was there any absorption of sulphur in residue A.

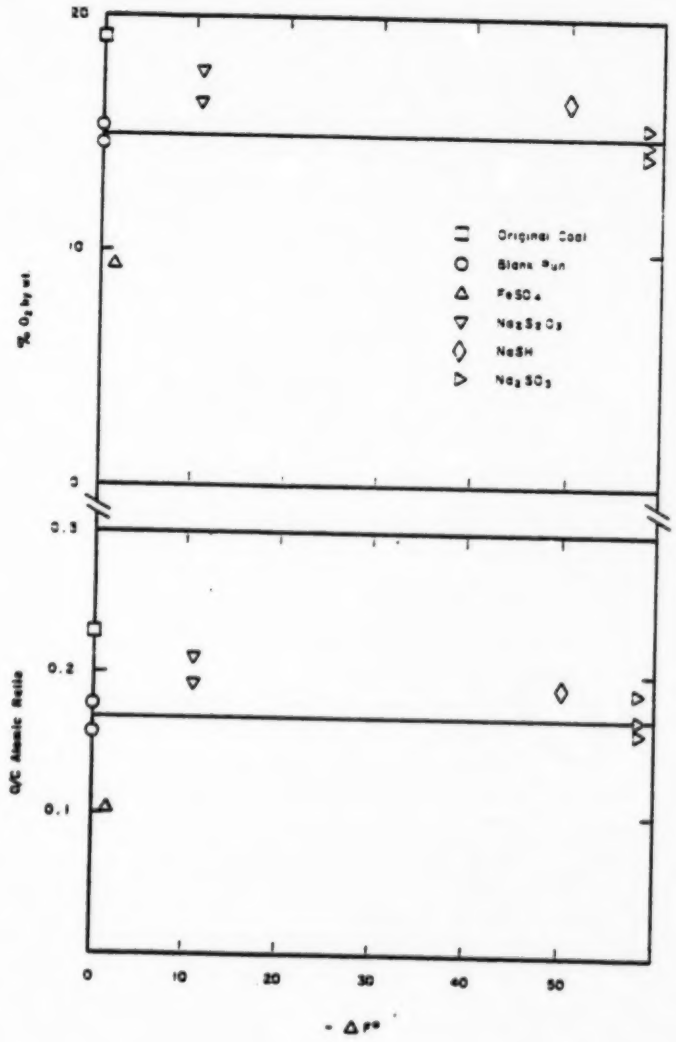


Figure 3 Graph of Oxygen wt% in Residue A and O/C Atomic Ratio Versus the Reducing Powers of the Reducing Agents for Lignitic Coal

Table 4 Liquid Products Yields for Hydrogenation Plant for Lignitic Coal

| Run No. | Red. Ag. | Temp. of Reduction °C | Hydrogenation Pressure psi | Hydrogen. Temp. °C | Wt. Res.A. g | Wt. Res.B. g | Wt. Res.C g | Yields Liquid % |
|---|---|---|---|---|---|---|---|---|
| 6 | None | - | 2500 | - | 50 | 37.3 | 9.3 | 18.6 |
| 33 | None | - | 2600 | 414 | 20 | 16.1 | 3.7 | 18.5 |
| 31 | $Na_2SO_3$ | 135-160 | 2200 | 408 | 20 | 19.0 | 0.5 | 2.5 |
| 29 | $Na_2SO_3$ | 240-260 | 2400 | 410 | 20 | 18.2 | 1.3 | 6.5 |
| 32 | $Na_2SO_3$ | 245-262 | 2400 | 414 | 20 | 16.1 | 3.7 | 18.5 |
| 15 | $Na_2S_2O_3$ | 146-159 | 2500 | 425 | 20 | 13.1 | 6.0 | 30.0 |
| 25 | $Na_2S_2O_3$ | 245-265 | 2400 | 418 | 20 | 18.1 | 1.7 | 8.5 |
| 19 | NaHS | 140-173 | 2300 | 412 | 20 | 16.7 | 2.7 | 13.5 |
| 21 | NaHS | 245-265 | 2300 | 400 | 20 | 18.2 | 1.3 | 6.5 |
| 16 | $FeSO_4$ | 148-227 | 2100 | 407 | 20 | 18.5 | 1.3 | 6.5 |
| 26 | $N_2H_4$ | 235-275 | 2700 | 420 | 20 | 18.5 | 1.4 | 7.0 |

Table 5 Amount of Composition of the Gaseous Products Generated in the Hydrogenation Runs for Lignitic Coal.

| Run No. | Red. Ag. | Temp. of Reduction $^{o}C$ | Gas Vol. Vented $ft^3$ | Gas Composition | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Water g | Methane % | Ethane % | Propane % | Iso-But. % | N-But. % |
| 6 | None | - | 15.2 | 0.64 | 46.7 | 31.1 | 17.1 | 1.5 | 3.4 |
| 33 | None | - | 18.3 | 0.21 | 23.0 | 26.2 | 41.2 | 3.7 | 5.9 |
| 31 | $Na_2SO_3$ | 135-160 | 17.3 | 0.27 | 29.0 | 10.0 | 57.1 | 2.1 | 1.8 |
| 29 | $Na_2SO_3$ | 240-260 | 17.3 | 0.22 | 49.3 | 7.9 | 36.8 | 4.4 | 1.5 |
| 32 | $Na_2SO_3$ | 245-262 | 19.0 | 0.14 | 63.8 | 6.8 | 14.2 | 6.2 | 8.9 |
| 15 | $Na_2S_2O_3$ | 146-159 | 16.4 | 0.23 | 31.5 | 34.8 | 23.3 | 2.0 | 8.3 |
| 25 | $Na_2S_2O_3$ | 245-265 | 17.5 | 0.25 | 13.5 | 4.7 | 61.2 | 16.0 | 4.7 |
| 19 | NaHS | 140-173 | 16.5 | 0.16 | 45.7 | 13.0 | 27.9 | 3.0 | 10.3 |
| 21 | NaHS | 245-265 | 15.5 | 0.20 | 33.8 | 6.4 | 47.8 | 17.5 | 4.4 |
| 16 | $FeSO_4$ | 148-227 | 12.5 | 0.18 | 29.5 | 29.8 | 34.5 | 1.4 | 4.7 |

Table 6 Hydrogen Balance for Lignitic Coal

| Run No. | Red. Ag. | Temp. of Reduction $^{o}C$ | H Residue A g | H Residue B g | H Residue C g | H Consumed g |
|---|---|---|---|---|---|---|
| 6 | None | - | 1.70 | 1.83 | 0.69 | 0.82 |
| 33 | None | - | 0.74 | 0.66 | 0.28 | 0.28 |
| 31 | $Na_2SO_3$ | 135-160 | 0.67 | 0.76 | 0.11 | 0.20 |
| 29 | $Na_2SO_3$ | 240-260 | 0.72 | 0.76 | 0.04 | 0.08 |
| 32 | $Na_2SO_3$ | 245-262 | 0.68 | 0.42 | 0.09 | (-0.17) |
| 15 | $Na_2S_2O_3$ | 146-159 | 0.78 | 0.47 | 0.43 | 0.12 |
| 25 | $Na_2S_2O_3$ | 245-265 | 0.76 | 0.65 | 0.15 | 0.04 |
| 19 | NaHS | 140-173 | 0.79 | 0.77 | 0.20 | 0.18 |
| 21 | NaHS | 245-265 | 0.80 | 0.75 | 0.11 | 0.06 |
| 16 | $FeSO_4$ | 148-227 | 0.82 | 0.70 | 0.08 | 0.04 |

Table 7 Analyses of Lignitic Coal Residues B and C

| Reducing Agent | Run No. | Residue | C % | H % | N % | O % |
|---|---|---|---|---|---|---|
| None | 6 | B | 61.8 | 4.9 | 0.9 | 5.9 |
| | | C | 79.4 | 7.4 | 1.1 | 7.2 |
| None | 33 | B | 61.6 | 4.1 | 1.5 | - |
| | | C | 84.8 | 7.6 | 1.6 | - |
| $Na_2SO_3$ | 31 | B | 59.3 | 4.0 | 1.3 | - |
| | | C | 78.3 | 8.6 | 1.0 | - |
| $Na_2SO_3$ | 29 | B | 61.5 | 4.2 | 1.4 | -- |
| | | C | 81.7 | 8.1 | 1.2 | -- |
| $Na_2SO_3$ | 32 | B | 34.5 | 2.3 | 0.7 | - |
| | | C | 83.2 | 7.7 | 1.4 | - |
| $Na_2S_2O_3$ | 15 | B | 56.0 | 3.6 | 0.7 | 10.2 |
| | | C | 84.4 | 7.1 | 1.3 | 5.1 |
| $Na_2S_2O_3$ | 25 | B | 58.6 | 4.3 | 1.2 | - |
| | | C | 81.4 | 8.8 | 0.9 | - |
| NaHS | 19 | B | 59.4 | 4.6 | 0.8 | 12.2 |
| | | C | 82.9 | 7.5 | 1.2 | 5.7 |
| NaHS | 21 | B | 58.3 | 4.1 | 1.3 | - |
| | | C | 82.1 | 8.8 | 1.1 | - |
| $FeSO_4$ | 16 | B | 68.7 | 3.8 | 1.0 | 6.2 |
| | | C | 88.3 | 6.5 | 0.9 | 4.0 |
| $N_2H_4$ | 26 | B | 64.2 | 4.1 | 4.2 | -- |
| | | C | 82.8 | 8.2 | 3.8 | -- |

## 3.0 RESULTS AND DISCUSSIONS (cont'd)

### 3.3.1 Treatment with water (blank run)

When lignite was heated in water the oxygen content of the coal decreased, whereas in bituminous coal, exactly the opposite phenomenon occured. The oxygen content increased (Figure 4, Table 8).

### 3.3.2 Treatment with NaSH in water

In this treatment,there was an even greater increase in oxygen found in the residue A than when the coal was just heated with water.

The only way in which oxygen could be added to the coal in these treatments is by the addition of water. Hydrolysis appears to be taking place. When heated with only water, partial hydrolysis might have taken place, while when heated with an aqueous solution of a strong base, more hydrolysis, probably complete hydrolysis, took place.

Stoichiometric calculations which are given in Appendix C indicate that there are 1.83 ester linkages for every 100 carbon atoms.

### 3.3.3 Treatment with $FeSO_4$ in water

In this treatment there was a substantial decrease in oxygen content of residue A. Here also, as in the case of lignite, this effect is attributed to the catalytic decarboxylation of coal. The consumption of $FeSO_4$ in runs 22 and 17 is negligible. However it should be pointed out that $FeSO_4$ data in this case are not quite consistent. Stoichiometric calculations made on the assumption that all the esters in coal are hydrolyzed and then carboxyl groups are catalytically removed by treatment with $FeSO_4$, indicate that there are 1.43 ester linkages for every 100 carbon atoms. This suggests that about 83% of the oxygen in bituminous coal is bound up in the ester group. Lowry (1)

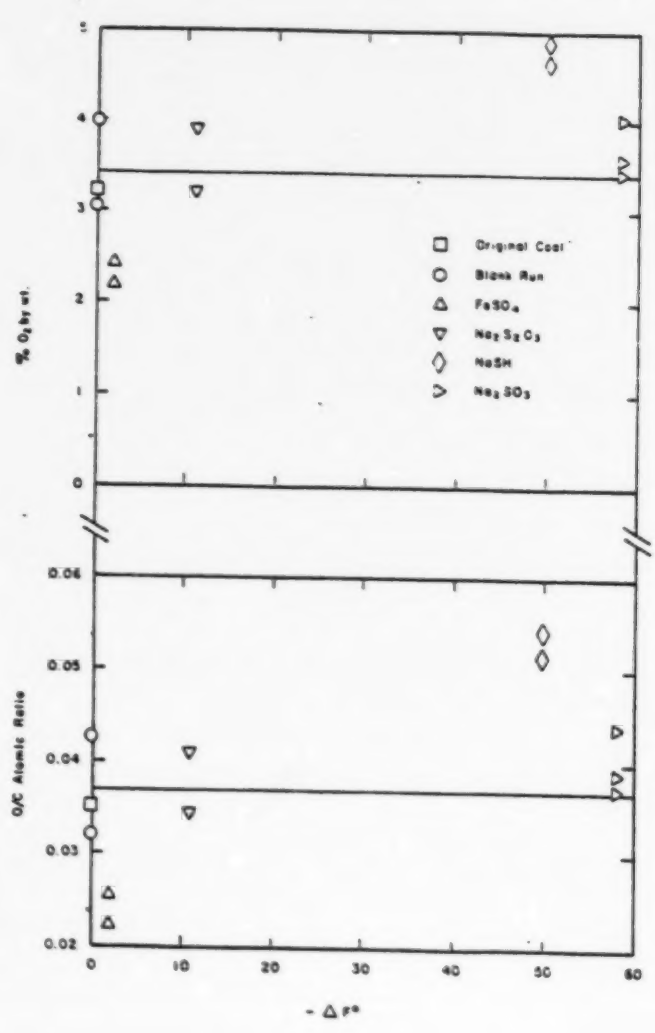


Figure 4 Graph of Oxygen wt% in Residue A and O/C Atomic Ratio Versus the Reducing Powers of the Reducing Agents for Bituminous Coal

Table 8 Deoxygenation Results for Bituminous Coal

| Run No. | Red. Ag. | Temp. of Reduction °C | Red. Ag. Consumed g | Analyses of Residue A, wt% | | | | | | O/C | H/C |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Ash | C | H | N | S | O(Diff) | Atomic | Atomic |
| Feed Coal | - | - | - | 21.4 | 69.9 | 3.84 | 1.1 | 0.3 | 3.23 | 0.035 | .66 |
| 7 | None | - | - | 19.4 | 71.7 | 4.2 | 1.0 | 0.5 | 3.1 | 0.032 | .70 |
| 30 | None | - | - | 19.9 | 70.3 | 4.2 | 1.0 | 0.5 | 4.0 | 0.043 | .72 |
| 5 | $Na_2SO_3$ | 150 | 62.3 | 22.615 | 67.82 | 4.05 | 1.01 | 0.5 | 4.0 | 0.044 | .72 |
| 8 | $Na_2SO_3$ | 250 | 9.0 | 20.7 | 69.7 | 4.2 | 1.1 | 0.5 | 3.6 | 0.039 | .72 |
| 9 | $Na_2SO_3$ | 143-176 | 1.7 | 21.4 | 69.6 | 4.1 | 1.0 | 0.5 | 3.5 | 0.038 | .71 |
| 14 | $Na_2S_2O_3$ | 145-165 | None | 21.0 | 70.1 | 4.1 | 1.0 | 0.5 | 3.2 | 0.034 | .70 |
| 24 | $Na_2S_2O_3$ | 245-265 | None | 19.7 | 70.6 | 4.1 | 1.1 | 0.5 | 3.9 | 0.041 | .70 |
| 22 | $FeSO_4$ | 148-227 | None | 19.84 | 70.1 | 4.2 | 1.1 | 0.5 | 4.2 | 0.045 | 72 |
| 17 | $FeSO_4$ | 140-169 | None | 19.7 | 71.7 | 4.6 | 1.0 | 0.5 | 2.5 | 0.026 | .77 |
| 23 | $FeSO_4$ | 245-265 | 5.14 | 19.9 | 72.0 | 4.4 | 1.0 | 0.5 | 2.2 | 0.023 | .73 |
| 18 | NaHS | 150-176 | 0.24 | 21.6 | 68.0 | 4.0 | 1.1 | 0.5 | 4.7 | 0.052 | .71 |
| 20 | NaHS | 250-275 | 0.02 | 21.0 | 68.4 | 4.0 | 1.1 | 0.5 | 4.9 | 0.054 | .70 |
| 27 | $N_2H_4$ | 235-250 | 19.1 | - | 72.3 | 4.3 | 1.3 | - | - | - | .71 |

3.0 RESULTS AND DISCUSSIONS (cont'd)

3.3.3 Treatment with $FeSO_4$ in Water (cont'd)

has reported that carbonyl and hydroxyl groups can account for only 10 to 30% of the oxygen. Hence, our value of Ester group in coal is in general agreement with the value reported in the literature. However, some of the recent papers (6, 7) have reported that in bituminous coals, the carbonyl and hydroxyl groups can account for as much as 30-40% of the oxygen. This indicates that other oxygen functionalities may have also been removed by the iron sulfate treatment, however, it will be overly speculative to draw any firm conclusion at this stage. This point should be investigated in the subsequent work. Calculations for the Ester group determination are shown in Appendix C.

3.3.4 Treatment with $Na_2S_2O_3$ and $Na_2SO_3$

In these treatments, no significant amount of oxygen was removed. The effect of hydrolysis reaction which was observed in the case of heating coal in water was also observed in these cases.

3.3.5 Treatment with Hydrazine

In the run where bituminous coal was treated with hydrazine, based on the reducing agent consumed, 38.2g of oxygen should have been removed. This is more than the original oxygen content and also more than the reduction in total weight.

Probably, however, some 15g (equivalent to the loss in others) of oxygen and 15g of hydrazine reacted. The extra 38.2 - 15 = 23.2g of hydrazine which disappeared remained with residue A and then was evaporated during the drying operation. This evaporation is suggested by the lack of nitrogen pick-up. The loss in hydrogen in approximately the same molal amount as the loss of oxygen, suggests that these two elements may have been removed together as hydroxyl groups.

Decomposition of reducing agent was observed in the $NaNO_2$ treatment of coal.

## 3.0 RESULTS AND DISCUSSIONS (Cont'd)

### 3.4 Hydrogenation Treatment

The residue A, derived after the deoxygenation treatment, was slurried with tetralin and was hydrogenated at 2500 psi pressure and about 400°C temperature. The results of hydrogenation treatment are presented in Tables 4 to 7 and Tables 9 to 12. In Table 4 and 9, weight of residue C represents the amount of liquid produced in the hydrogenation. Based on this weight the liquid yield was calculated. Residue B would consist of unconverted coal and solvent refined coal (SRC). The amount of SRC in residue B was not determined, hence it is not possible to calculate the coal conversion that took place in the hydrogenation treatment. None of the parameters such as water content in gaseous products (Tables 5 and 10), hydrogen consumption calculated based on hydrogen balance (Tables 6 and 11) and the hydrogen content of residue B and C (Tables 7 and 12) reveal any clear variation or trend that could be correlated to the type of reducing agent employed in the deoxygenation treatment. Thus, it appears that these results are of little value in evaluating the efficacy of the reducing agents employed in the deoxygenation treatment.

Table 9 Liquid Products Yields for Hydrogenation Runs for Bituminous Coal

| Run No. | Red. Ag. | Temp. of Reduction °C | Hydrogenation Pressure psi | Hydrogen. Temp. °C | Wt. Res.A. g | Wt. Res.B g | Wt. Res.C g | Yields Liquid % |
|---|---|---|---|---|---|---|---|---|
| 7 | None | - | 2500 | - | 50 | 38.6 | 7.7 | 15.4 |
| 30 | None | - | 2500 | 410 | 20 | 15.5 | 4.0 | 20.0 |
| 5 | $Na_2SO_3$ | 150 | 2500 | - | 41 | 28.5 | 10.1 | 24.6 |
| 8 | $Na_2SO_3$ | 250 | 2300 | 418 | 20 | 15.6 | 3.3 | 16.5 |
| 9 | $Na_2SO_3$ | 143-176 | 2400 | 420 | 20 | 16.7 | 2.8 | 14.0 |
| 14 | $Na_2S_2O_3$ | 145-165 | 2300 | 422 | 20 | 16.6 | 3.6 | 18.0 |
| 24 | $Na_2S_2O_3$ | 245-265 | 2400 | 419 | 20 | 17.2 | 1.5 | 7.5 |
| 22 | $FeSO_4$ | 148-227 | 2300 | 408 | 20 | 17.4 | 1.7 | 8.5 |
| 17 | $FeSO_4$ | 140-169 | 2300 | 416 | 20 | 15.2 | 3.5 | 17.5 |
| 23 | $FeSO_4$ | 245-265 | 2400 | 406 | 20 | 17.1 | 1.3 | 6.5 |
| 18 | NaHS | 150-176 | 2300 | 405 | 20 | 16.2 | 2.9 | 14.5 |
| 20 | NaHS | 250-275 | 2400 | 424 | 20 | 17.9 | 1.1 | 5.5 |
| 27 | $N_2H_4$ | 235-250 | 2400 | 408 | 20 | 17.9 | 1.7 | 8.5 |

Table 10 Amount and Composition of the Gaseous Products Generated in the Hydrogenation Runs for Bituminous Coals

| Run No. | Red. Ag. | Temp. of Reduction °C | Gas Vol. Vented $ft^3$ | Water g | Gas Composition Methane % | Ethane % | Propane % | Iso-But. % | N-But. % |
|---|---|---|---|---|---|---|---|---|---|
| 7 | None | - | 16.3 | 0.37 | 57.9 | 26.9 | 11.2 | 1.0 | 2.9 |
| 30 | None | - | 17.5 | 0.12 | 13.5 | 19.9 | 64.7 | 0.8 | 1.0 |
| 5 | $Na_2SO_3$ | 150 | 18.9 | - | 43.7 | 28.2 | 19.5 | 1.5 | 7.0 |
| 8 | $Na_2SO_3$ | 250 | 14.2 | 0.40 | 42.3 | 44.7 | 12.9 | - | - |
| 9 | $Na_2SO_3$ | 143-176 | 15.9 | 0.21 | 40.5 | 36.2 | 23.3 | - | - |
| 14 | $Na_2S_2O_3$ | 145-165 | 14.4 | 0.13 | 49.2 | 25.2 | 25.0 | 0.2 | 0.4 |
| 24 | $Na_2S_2O_3$ | 245-265 | 17.3 | 0.02 | 11.7 | 11.2 | 71.2 | 4.9 | 1.1 |
| 22 | $FeSO_4$ | 148-227 | 14.2 | 0.05 | 7.5 | 8.1 | 69.1 | 12.1 | 3.1 |
| 17 | $FeSO_4$ | 140-169 | 13.7 | 0.31 | 33.7 | 23.9 | 25.5 | 2.7 | 9.1 |
| 23 | $FeSO_4$ | 245-265 | 17.6 | 0.17 | 25.7 | 13.8 | 38.0 | 17.9 | 4.6 |
| 18 | NaHS | 150-176 | 13.6 | 0.11 | 29.7 | 26.8 | 33.9 | 3.1 | 6.5 |
| 20 | NaHS | 250-275 | 16.86 | 0.15 | 44.2 | 14.5 | 26.9 | 4.0 | 10.4 |

Table 11 Hydrogen Balance for Bituminous Coal

| Run No. | Red. Ag. | Temp. of Reduction °C | H Residue A g | H Residue B g | H Residue C g | H Consumed g |
|---|---|---|---|---|---|---|
| 7 | None | - | 2.10 | 1.90 | 0.61 | 0 41 |
| 30 | None | - | 0.84 | 0.69 | 0.26 | 0.11 |
| 5 | $Na_2SO_3$ | 150 | 1.64 | 1.48 | 0.60 | 0.44 |
| 8 | $Na_2SO_3$ | 250 | 0.84 | 0.66 | 0.23 | 0.05 |
| 9 | $Na_2SO_3$ | 143-176 | 0.82 | 0.65 | 0.18 | 0.01 |
| 14 | $Na_2S_2O_3$ | 145-165 | 0.82 | 0.83 | 0.22 | 0.20 |
| 24 | $Na_2S_2O_3$ | 245-265 | 0.82 | 0.80 | 0.13 | 0.11 |
| 22 | $FeSO_4$ | 148-227 | 0.84 | 0.80 | 0.12 | 0.08 |
| 17 | $FeSO_4$ | 140-169 | 0.92 | 0.81 | 0.27 | 0.16 |
| 23 | $FeSO_4$ | 245-265 | 0.88 | 0.91 | 0.09 | 0.12 |
| 18 | NaHS | 150-176 | 0.80 | 0.58 | 0.20 | (-0.02) |
| 20 | NaHS | 250-275 | 0.80 | 0.81 | 0.07 | 0.08 |

Table 12 Analyses of Bituminous Coal Residues B and C

| Reducing Agent | Run No. | Residue | C % | H % | N % | O % |
|---|---|---|---|---|---|---|
| None | 7 | B | 83.8 | 5.1 | 1.2 | 4.4 |
| | | C | 88.5 | 6.6 | 1.0 | -- |
| None | 30 | B | 69.0 | 4.3 | 1.0 | -- |
| | | C | 84.6 | 6.9 | 1.0 | -- |
| $Na_2SO_3$ | 5 | B | 66.6 | 5.2 | 0.6 | 6.8 |
| | | C | 81.5 | 5.9 | 0.9 | 4.7 |
| $Na_2SO_3$ | 8 | B | 67.6 | 4.2 | 0.7 | 4.4 |
| | | C | 87.3 | 7.1 | 1.2 | -- |
| $Na_2SO_3$ | 9 | B | 65.5 | 3.9 | 0.8 | 4.6 |
| | | C | 87.7 | 6.4 | 1.1 | 4.3 |
| $Na_2S_2O_3$ | 14 | B | 74.0 | 5.0 | 0.7 | 3.7 |
| | | C | 84.4 | 6.1 | 0.7 | 3.5 |
| $Na_2S_2O_3$ | 24 | B | 65.0 | 4.6 | 1.2 | -- |
| | | C | 82.4 | 8.7 | 1.0 | -- |
| $FeSO_4$ | 22 | B | 71.2 | 4.6 | 1.1 | -- |
| | | C | 88.8 | 7.2 | 1.1 | -- |
| $FeSO_4$ | 17 | B | 61.6 | 5.3 | 0.8 | 7.2 |
| | | C | 85.0 | 7.8 | 1.6 | - |
| $FeSO_4$ | 23 | B | 70.8 | 4.9 | 0.9 | - |
| | | C | 88.2 | 6.8 | 0.9 | - |
| NaHS | 18 | B | 65.5 | 3.6 | 0.8 | 5.4 |
| | | C | 86.2 | 7.0 | 1.0 | 3.9 |
| NaHS | 20 | B | 70.0 | 4.5 | 1.0 | -- |
| | | C | 86.6 | 6.7 | 1.1 | -- |
| $N_2H_4$ | 27 | B | 76.1 | 4.6 | 1.3 | - |
| | | C | 88.0 | 7.1 | 1.2 | - |

## 4.0 CONCLUSIONS

Following conclusions can be drawn from the present investigation. Some of the conclusions may sound speculative and may need more experimentation for their confirmation.

1) Heating lignite with water in the range of 150 - 250°C results in partial decarboxylation of the material.

2) Heating lignite with an aqueous solution of ferrous sulphate in the range 150° - 250°C results in greater oxygen removal because of selective decarboxylation.

3) Heating lignite with aqueous solutions of various reducing agent gives essentially the same amount of oxygen removal as heating in water alone. It can be concluded that the reducing agents themselves have no effect.

4) Lignitic coal reacts strongly to bind the sulphur in the reducing agents to the coal molecule.

5) Heating bituminous coal with water in the range of 150 - 250°C results in the addition of oxygen. This can only be explained by partial hydrolysis of the ester linkages in the coal.

6) Heating bituminous coal in an aqueous solution of sodium hydrogen sulphide (a strong base) in the range of 150 - 250°C results in the addition of even greater amounts of oxygen. This may be due to the complete hydrolysis of the ester linkages in the coal.

7) Heating bituminous coal in an aqueous solution of ferrous sulphate results in a large decrease in the oxygen content. This may be explained by complete hydrolysis of the ester linkages and subsequent decarboxylation as was observed in the case of lignite.

## 4.0 CONCLUSIONS

8) Bituminous coal, in marked difference to lignite, does not react significantly with the sulphur in the reducing agent.

9) The inorganic reducing agents also have no effect on bituminous coal.

## 5.0 RECOMMENDATIONS FOR FURTHER WORK

At this point, it has to be reiterated that this investigation was exploratory in nature and that the extent of the work was rather modest. The results indicate that the ferrous ion acts catalytically to substantially decarboxylate all the acidic groups in both lignite and bituminous coal. The observation reported in the literature (5, 8, 9, 10) that copper ions catalytically decarboyxlate aromatic acids is a similar finding.

In view of these observations, we recommend that a study be carried out to ascertain the catalytic effect of various metal ions, such as iron, copper, tin, etc. in deoxygenating coal. This can be done by measuring the oxygen functional groups in the feed coals and the reaction product (Residue A). This will enable us to determine the oxygen functional groups selectively removed by the catalytic effect of metal ions. Also, this will confirm our findings of the present report.

The second recommendation which would lead to an exploratory study is to oxydize the carbonyl functional groups in coal. It is well known that carbonyl groups can be oxidized to carboxyl groups by various oxidizing agents such as potassium permanganate. It has been reported in the literature (1) that a large percentage of oxygen in coal is bound up in the carbonyl groups.

Hence, a two step method which would oxidize these carbonyl groups to carboxyl groups, which are then removed by the action of metal ion, would remove as much as 70% of the oxygen originally found in coal and hence, would offer a great economic advantage for the utilization of low rank coals.

## 5.0 RECOMMENDATIONS FOR FURTHER WORK (cont'd)

Hence, we recommend that tests be carried out to explore the possibility of oxidizing the carbonyl groups in coal to carboxyl groups by treating with various oxidizing agents.

The experimental finding in the present report, which suggests that the reducing agent did not remove any oxygen, indicates that no further work be done on that approach.

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# APPENDIX A

## SAMPLE CALCULATIONS FOR THE CORRECTION OF RESIDUE A ANALYSIS

Calculations for correction of analysis of Residue A because of retained reducing agent.

Basis: 100 gms of Residue A free of reducing agent, $A^* = W_A^*$

Let the weight of reducing agent retained be X gm.

The analysis of residue A for blank runs were treated as true analysis of Residue A. Hence, the corrections were made with respect to average blank run analysis.

Analysis of blank runs are given as follows:

| Run | 6 | 33 | Average |
|---|---|---|---|
| Ash | 13.00 | 13.75 | 13.375 |
| C | 66.60 | 65.30 | 65.950 |
| H | 4.00 | 3.71 | 3.855 |
| N | 1.30 | 1.30 | 1.300 |
| S | 0.54 | 0.55 | 0.545 |
| O (by diff) | 14.60 | 15.30 | 14.975 |

Define factors $F_a$ and $F_s$. While determining ash, the reducing agent trapped in Residue A was assumed to have oxidized.

$$X \xrightarrow{O} Y$$

Then $$F_a = \frac{Y}{X} = \frac{\text{M.W. of oxidation product in ash}}{\text{M.W. of reducing agent in ash}}$$

$F_a$ represents weight gain (or loss) because of oxidation of reducing agent while determining ash content of Residue A.

$$F_s = \frac{\text{M.Wt. of sulphur in reducing agent}}{\text{M.Wt. of reducing agent}} = \frac{M.W.s}{M.W.a}$$

Now, look at the actual calculations. The total weight of Residue A = $W_{A*} + X$

$= 100 + X$

Analysis of Residue A:

| | | A* | + | Added by reducing agent |
|---|---|---|---|---|
| Ash | = | 13.375 | + | $F_aX$ |
| C | = | 65.950 | | |
| H | = | 3.855 | | |
| N | = | 0.545 | + | $F_sX$ |
| O | = | 14.975 | | |

∴ By Ash Balance,

$$A' (100 + X) = 13.375 + F_aX \quad (1)$$

where $A'$ = fraction of ash in the analysis of Residue A

∴ From equation (1) by rearranging

$$X_A = \frac{100\,A' - 13.375}{F_a - A'} \quad (2)$$

∴ By sulphur balance

$$S' (100 + X) = 0.545 + F_sX \quad (3)$$

where $S'$ = fraction of sulphur in the analysis of Residue A.

∴ Rearrranging equation (3)

$$X_s = \frac{100S' - 0.545}{F_s - S'} \quad (4)$$

Hence, there are two independent equations to calculate reducing agent bound to the coal (eq. 2 and 4).

$X_S$ and $X_A$ should be close to each other. The value of $X_A$ which is closest to the value of $X_S$ would indicate the type of oxidation reaction occuring while determining ash.

The oxygen is determined by difference. The value of $X_s$ will be used to determine the correction. The corrected value of ash will be forcibly brought to the weight of ash in blank runs.

.. Corrected values are as follows:

$$A^* = A' (100 + X_s) - F_a X_s = 13.375$$
$$C^* = C' (100 + X_s)$$
$$H^* = H' (100 + X_s)$$
$$N^* = N' (100 + X_s)$$
$$S^* = S' (100 + X_s) - F_s X_s = 0.545$$
$$O^* = 100 - (A' + C' + H' + N' + S') (100 + X_s) - F_s X_s - 13.375$$

For example Run 31, reducing agent - $Na_2SO_3$

Two values of $X_A$ will be calculated depending of two different oxidation products. Then, based on the value of $X_s$ the true oxidation product in the ash will be determined.

$$Na_2SO_3 \xrightarrow{0} Na_2O \quad \text{(i)}$$
$$Na_2SO_3 \xrightarrow{0} Na_2SO_4 \quad \text{(ii)}$$

$F_a$ (i) = 0.492

and $F_a$ (ii) = 1.127

$F_s$ in both cases is = 0.254

$X_s$ = 9.013

$X_a$(i) = 28.54

$X_a$(ii) = 8.706

Hence, $Na_2SO_3$ appears to be getting converted to $Na_2SO_4$ while determining the ash content of Residue A.

∴ The corrected analysis of Residue A:

| | | |
|---|---|---|
| A* | = 0.2133 (109.013) - 9.013 (1.127) - 13.08 ⟶ | 13.375 |
| C* | = 0.616 (109.013) | = 67.15 |
| H* | = 0.32 (109.013) | = 3.49 |
| N* | = 0.0135 (109.013) | = 1.47 |
| S* | = 0.026 (109.013) - 9.013 (0.254) | = 0.55 |
| O* | (by difference) | = 13.97 |
| O/C | atomic ratio | = 0.156 |

Similarly, other analyses were corrected. Corrected analyses are listed in Table 3 of the main text.

# APPENDIX B

## SAMPLE CALCULATIONS TO DETERMINE THE AMOUNT OF CARBOXYL OXYGEN IN COAL

Calculations for the determination of the percentage of the carboxyl oxygen in the lignite.

It is assumed that only carboxyl oxygen (-COOH) is removed in blank runs and in the runs where coal is treated with $FeSO_4$ solution. Therefore, for every atom of carbon, two oxygen atoms are removed.

Basis: 100 carbon atoms in the original coal.

O/C ratio in feed coal = 0.231
Average O/C ratio after blank runs = 0.170
O/C ratio after run 16 ($FeSO_4$) = 0.102 (corrected)

$\therefore$ By oxygen balance (blank run)

$$\frac{23.0 - 2X}{100 - X} = 0.17 \qquad (1)$$

$\therefore$ $X = 3.33$

% O removed $= \frac{6.66}{23.1} = 28.8\%$

Oxygen balance Run 16 ($FeSO_4$)

$$23.1 - 2X = 0.102\ (100 - X) \qquad (2)$$

$\therefore$ $X = 6.797$

% oxygen $= \frac{13.59}{23.1} = 58.8\%$

Thus, amount of oxygen removed in Run 16 indicates that 58.8% oxygen in coal is in the form of carboxyl groups.

Hence, percentage carboxyl groups removed in the blank run is:

$$= \frac{28.8}{58.8} \times 100$$

$$= 48\%$$

# APPENDIX C

## CALCULATIONS OF ESTER GROUPS IN THE BITUMINOUS COAL

Calculations of ester groups in coal are carried out by making the two following assumptions.

1. Treatment with NaSH hydrolyzes all the ester groups present in coal.
2. Treatment with $FeSO_4$ also hydrolyzes all the ester groups in coal and catalytically removes all the carboxyl groups present in coal.

O/C ratio with original coal = 0.0346 (Note all ratios are atomic ratios).
Basis - 100 carbon atoms
After treatment with NaSH solution,

$$\text{average O/C ratio} = \frac{0.052 + 0.0537}{2}$$

$$= 0.0529$$

∴ There are 5.29 oxygen atoms per 100 carbon atoms after treatment
∴ Oxygen atoms added = 5.29-3.46 = 1.83

∴ For every 100 carbon atoms 1.83 molecules of $H_2O$ are added.
∴ 3.66 atoms of H are added.

A check can be carried out by determining the H atoms added from the experimental data.

H/C ratio in the original coal = 0.659
H/C ratio after treatment with NaSH = 0.704
H atoms added = 70.4-65.9 = 4.5

The value 4.5 atoms of hydrogen added by hydrogen balance compares favorably with 3.66 atoms of hydrogen added by the oxygen balance.

- After treatment with $FeSO_4$

$$O/C = \frac{0.0262 + 0.0230}{2} = 0.0246$$

Let X carbonyl groups removed by the treatment then 2 X oxygen atoms removed and X carbon atoms removed

$\therefore$ By oxygen balance,

$(100-X)\ 0.0246 = 5.29-2X$

$\therefore$ $X = 1.43$

$\therefore$ Number of carboxyl groups removed by decarboxylation are = 1.43

Now every carboxyl group comes from one ester group hydrolyzed.

$\therefore$ Ester groups in coal are $= \frac{1.43}{100}$ atoms of carbon

Each ester contains two oxygen atoms.

$\therefore$ Oxygen atoms in esters are = 2.85 atoms per 100 carbon atoms

$\therefore$ % ester groups in coal $= \frac{2.86}{3.46} \times 100 = 82\%$

Hence only 17.3% of oxygen is bound in the carbonyl and hydroxyl groups. The literature value for the contribution of oxygen due to these two groups combined is 10-30%.